Spin-dependent tunneling and Coulomb blockade in ferromagnetic nanoparticles

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Abstract

In this paper we review studies on spin-dependent transport in systems containing ferromagnetic nanoparticles. In a tunnel junction with a nanometer-scale-island, the charging effect leads to an electric current blockade phenomenon in which a single electron charge plays a significant role in electron transport, resulting in single-electron tunneling (SET) properties such as Coulomb blockade and Coulomb staircase. In a tunnel junction with a ferromagnetic nano-island and electrode, it was expected that the interplay of spin-dependent tunneling (SDT) and single-electron tunneling (SET), i.e., spin-dependent single-electron tunneling (SD-SET), would give rise to remarkable tunnel magnetoresistance (TMR) phenomena. We investigated magnetotransport properties in both sequential tunneling and cotunneling regimes of SET and found the enhancement and oscillation of TMR. The self-assembled ferromagnetic nanoparticles we have employed in this study consisted of a Co-Al-O granular film with cobalt nanoparticles embedded in an Al-O insulating matrix. A $Co_{36}Al_{22}O_{42}$ film prepared by a reactive sputtering method produced a TMR ratio reaching 10 % and superparamagnetic behavior at room temperature. The TMR ratio exhibited an anomalous increase at low temperatures but no indication of change with bias voltage. In Ch. 4, we show that the anomalous increase of the MR provided evidence for higher-order tunneling (cotunneling) between large granules through intervening small granules. We emphasize that the existence of higher-order tunneling is a natural consequence of the granular structure, since broad distribution of granule size is an intrinsic property of granular systems. In Ch. 5, we concentrate on SD-SET properties in sequential tunneling regimes. We fabricated two types of device structures with Co-Al-O film using focused ion-beam milling or electron-beam lithography techniques. One had a granular nanobridge structure: point-shaped electrodes separated by a very narrow lateral gap filled with the Co-Al-O granular film. The other had a current-perpendicular-to-plane (CPP) geometry structure: a thin Co-Al-O granular film sandwiched by ferromagnetic electrodes with the current flowing in the direction perpendicular to

the film plane through a few Co particles. We found the enhancement and oscillation of TMR due to spin-dependent SET in sequential tunneling regimes. In Ch. 6, we report experimental evidence of a spin accumulation effect in Co nanoparticles leading to the oscillation of TMR with alternate sign changes. Furthermore, we discovered that the spin relaxation time in the nanoparticles is unprecedentedly enhanced up to the order of more than hundreds of nanoseconds, compared to that evaluated from the spin-diffusion length of ferromagnetic layers in previous CPP-GMR studies, *i.e.*,the order of tens of picoseconds.

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1. Introduction

Ever Since the giant magnetoresistance (GMR) effect was discovered in 1988[1], magnetotransport phenomena in magnetic multilayers with precise layer-by-layer deposition on a nanometer scale have attracted much attention due to the potential applications of large magnetoresistance. GMR and Tunnel magnetoresistance (TMR)[2-4] discoveries have raised physical issues regarding the interplay between the spin and charge of an electron. From the industrial point of view, the control of this interplay is important because larger magnetoresistance is key to higher performance of data storage applications[5-8].

Progress in microfabrication technique has enabled us to study characteristic phenomena in laterally small sizes, and it has long been known in metallic or semiconductor systems, nanometer-sized structures provide insight into mesoscopic phenomena such as quantization of conductance, single-electron tunneling, discreteness of the chemical potentials, and so on. To study a mesoscopic property, we must reduce the size of a structure within a characteristic length according to its feature and temperature. For example, to study Coulomb blockade and resulting single-electron tunneling (SET) properties at room temperature, the size of a particle should be less than 3 nm (embedded in a vacuum) [9]. A microstructure a few nanometer in size, which is under the microfabrication limit, is generally prepared by a bottom-up process.

Returning to the magnetic systems, and in view of GMR or TMR in layered nanostructures, it has naturally been anticipated that spin-dependent transport in three-dimensional magnetic nanostructures would gives rise to further novel phenomena. Our interest emerged especially in the interplay of spin-dependent tunneling (SDT) and SET in magnetic nanoparticles. TMR, which was discovered in 1995[3, 4], has normally been studied in magnetic tunnel junctions (MTJs) consisting of a 1-3 nm-thick insulating barrier layer sandwiched between upper and lower ferromagnetic electrodes, and its ratio is given by the difference in the electrical resistance between parallel and anti-parallel alignments of magnetization vectors. The TMR ratio of a macroscopic MTJ with an amorphous insulating barrier is almost consistent with that proposed by Julliere [10] in terms of the spin polarizations of the electrodes. In the case that the size of the MTJs is reduced to nanometer-scale, the interplay of SDT and SET causes a peculiarity in the TMR ratio different from that of the Julliere model.

Here we report characteristic magnetotranport behaviors arising from the interplay of SDT and SET in samples using magnetic nanoparticles. We employed an insulating granular film consisting of a few nanometer-sized magnetic particles embedded in an insulating matrix. The size of the particles was so small that their charging energy exceeds 30 meV ($\sim$300 K), in which case SET is expected to occur between pairs of neighboring particles at low temperatures. In a granular film of macroscopic size containing a large number of particles, however, SET phenomena between neighboring particles average out, due to the large distribution of particle sizes and interparticle distances. In order to observe SET phenomena such as Coulomb staircase and Coulomb blockade with a clear threshold, the tunnel paths must be restricted from among the vast number of

possible paths by uniting them with microfabricated electrodes.

First, we describe characteristic magnetotransport behavior in non-microfabricated granular films. Although SET properties average out in non-microfabricated samples, the higher-order tunneling process in a Coulomb blockade regime, or so-called cotunneling, gives rise to enhanced TMR at a low-temperature and low-bias-voltage region. Next, we describe magnetotranport behavior for microfabricated granular films. The microstructures using granular film we prepared in this study consisted of either a granular nanobridge or a granular CPP (current-perpendicular-to-plane) structure. In the former, or lateral-type microstructure, a granular film was placed in a nanogap of microfabricated electrodes. We found enhanced TMR associated with Coulomb blockade in this structure. The latter was a nanopillar of layered structure: in this case, a granular film was sandwiched between electrodes. In the CPP structure, we found interesting TMR behavior due to SET and spin accumulation in nanoparticles; in addition, it was elucidated that spin relaxation time is much enhanced in the Co nanoparticles.

2. Basic concepts

2.1 Spin-dependent tunnel magnetoresistance

Tunnel magnetoresistance (TMR) originates from spin-dependent tunneling in an FM / I / FM magnetic tunnel junction (MTJ), where the FMs are ferromagnetic layers and the I is a tunnel barrier that is a few nm thick. In 1975, Julliére formulated a model for the difference in conductance between the parallel and anti-parallel configurations in the two FM electrodes, FM1 and FM2. TMR is defined as:

$$\mathrm{TMR} = \frac{\Delta R}{R_P} = \frac{R_{AP} - R_P}{R_P} = \frac{G_P - G_{AP}}{G_{AP}}, \tag{2.1}$$

where $R_{P(AP)}$ is the resistance and $G_{P(AP)}$ is the conductance for the P (AP) alignment [10]. G is given from the sum of the G for each spin channel σ, and G_σ is described by

$$G_\sigma \propto \sum D_{1\sigma} D_{2\sigma}, \tag{2.2}$$

where $D_{1(2)\sigma}$gs the density of states of the σ spin channel at the Fermi level in FM1(FM2). The total conductance in the P alignment is given by

$$G_P = G_P^{\uparrow} + G_P^{\downarrow} \propto D_{M1} D_{M2} + D_{m1} D_{m2}, \tag{2.3}$$

and in the AP alignment

$$G_{AP} = G_{AP}^{\uparrow} + G_{AP}^{\downarrow} \propto D_{M1} D_{m2} + D_{m1} D_{M2}, \tag{2.4}$$

where D_{Mi} and D_{mi} are the densities of states for the majority and minority spin bands in the i-th FM electrode, respectively. The spin polarization of the i-th electrode is defined by

$$P_i = \frac{D_{Mi} - D_{mi}}{D_{Mi} + D_{mi}}. \tag{2.5}$$

Using this definition, Eq. (2.1) can be expressed as

$$\mathrm{TMR} = \frac{G_P - G_{AP}}{G_{AP}} = \frac{2P_1 P_2}{1 - P_1 P_2}. \tag{2.6}$$

According to Eq. (2.6), which was predicted by Julliére, a TMR of about 28 % is expected assuming both electrodes are Co with P $\sim$ 0.35. This prediction of the Julliére model almost exactly reflects the experimental results for MTJs with Al-O amorphous barriers.

In the case of insulating granular systems, we normally define the TMR ratio as TMR = $\Delta R/R_{max}$. The TMR ratio should be smaller than those of MTJs because of the random orientation of the magnetization (M) at the zero field resulting in an incomplete anti-parallel configuration. Inoue and Maekawa

considered the relative magnetization of a granular system $m = M \ / \ M_s$, where M_s is the saturation magnetization, and derived the TMR as [11]:

$$\text{TMR} = \frac{m^2 P^2}{1 + m^2 P^2}. \tag{2.7}$$

Assuming Co nanoparticles with P$\sim$0.35, the saturated ($m = 1$) TMR ratio $P^2/(1+P^2)$ is evaluated to be about 11 %.

2.1 Charging effect of nanoparticles

The charging effect of nanoparticles leads to a Coulomb blockade; then the single-electron charge plays a significant role in electron transport [9, 12, 13]. A simplified model is shown in Fig. 2-1: an individual particle, isolated in an insulating barrier, is located between source and drain electrodes, and the tunneling electron travels from the source to the drain through the particle. The tunneling of electrons can be inhibited, and the current does not flow at small bias voltages if the electrostatic energy $e^2/2C$ of a single excess electron on the island is much larger than the thermal energy $k_B T$, where C is the capacitance of the island. The suppression of current at small bias voltages is called a Coulomb blockade. When the bias voltage increases and exceeds the threshold $V_{th} = e/2C$, the current starts to increase. If one junction resistance is similar to that of other ($R_1 \approx R_2$), the current increases smoothly with bias voltage (see Fig. 2-2 (a)). On the other hand, if the difference between the two junction resistances is very large ($R_1 << R_2$or $R_1 >> R_2$), the current increases stepwise with bias voltage depending on the number of electrons accumulated on the island (see Fig. 2-2 (b)). The step-like structure in current vs. bias-voltage ($I - V_b$) characteristics is called the Coulomb staircase. The Coulomb blockade and the Coulomb staircase are representative phenomena of single-electron tunneling (SET). In practice, even for multiple junctions including not only one but some islands between electrodes, SET phenomena can be observed.

For the appearance of SET phenomena, the following two conditions are generally essential. First, as mentioned above, the charging energy E_c required to add an electron to an island must far exceed the thermal energy; i. e.,

$$E_c >> k_B T. \tag{2.8}$$

Second, the junction resistance R_J must exceed the resistance quantum $R_K = h/e^2 \approx$25.8 kΩ; i. e.,

$$R_J >> R_K, \tag{2.9}$$

which ensures that the wave function of an excess electron on an island is localized there. Without this condition, the electron would be delocalized through the island, permitting the transport. SET phenomena in nonmagnetic systems, where both islands and electrodes are nonmagnetic, have been extensively investigated, both theoretically and experimentally [9]. The islands must be small enough to satisfy Eq. (2.8), since E_c increases as the island size decreases. The

E_c of an isolated island is described as

$$E_c = e^2/4\pi\varepsilon d, \tag{2.10}$$

where d is the diameter assuming the island is a sphere, and ε is the dielectric constant of an insulator around the island. Although E_c is somewhat modified by the configuration of surrounding islands and electrodes in a real system, we may consider that E_c is roughly proportional to $1/d$. The E_c for submicron-sized islands is generally of the order of 10^{-4}-10^{-3} eV (1∼10 K). Thus, SET phenomena can be observed only at very low temperatures.

There are two distinct tunneling processes by which electrons are transferred between the electrodes via a small island: sequential tunneling and cotunneling. In sequential tunneling, there is no correlation between tunneling events into and out of the island. In this process, electron tunneling in either of the two junctions causes an increase of charging energy, and is suppressed by a Coulomb blockade. However, cotunneling occurs when tunnel resistance is not so high (1 or 2 orders higher) compared to the resistance quantum ($R_K \sim 25.8$ kΩ). In the cotunneling process, two electrons tunnel in a correlated fashion, i.e., an electron tunnels into the island while the second electron simultaneously leaves the island through the other junction; the island is only virtually charged in this cotunneling process, and therefore there is no increase in charging energy in the overall tunneling process. Therefore, the cotunneling process contributes to a finite current even in a Coulomb blockade regime.

2.2 Spin-dependent single-electron tunneling

In the last section, we neglected the spin degree of freedom. In the magnetic tunnel junctions, the tunnel current depends on the relative orientation of magnetizations in the ferromagnetic electrodes. Assuming a double tunnel junction model with a ferromagnetic nanoparticle put between ferromagnetic electrodes, it was expected that the interplay of spin-dependent tunneling (SDT) and single-electron tunneling (SET), so called spin-dependent single-electron tunneling (SD-SET), would give rise to remarkable tunnel magnetoresistance (TMR) phenomena.

Magnetotransport properties have been studied in both sequential tunneling and cotunneling regimes. In the limit of the sequential regime, phenomena are discussed in the framework of the orthodox theory of SET. Pioneering theoretical studies were performed by Barnas and Fert [14, 15], and Majumdar and Hershfiled [16] in 1998. They predicted that novel TMR behaviors such as modification of the spin-dependent tunneling probability associated with Coulomb staircase give rise to a TMR peak around the step point of the staircase. A peak appears at each step resulting in the oscillation of TMR as a function of the bias-voltage. Following their studies, further analyses were made by several authors [17-36]. Some studies have considered SD-SET with additional effects such as spin accumulation [17-30, 36] and a discrete energy spectrum [20, 32-34] in the island. Characteristic TMR behavior due to the spin accumulation effect was

predicted: the difference in the spin-splitting of the chemical potential between parallel and anti-parallel alignment of magnetic vectors gives rise to an alternate sign change of TMR [15, 27, 28, 30, 37]. The spin accumulation effect has been mainly considered in an SET device model with a nonmagnetic nano-island placed between ferromagnetic electrodes. Although TMR should not appear in the framework of the Julliére model, nonequilibrium magnetic polarization due to spin accumulation leads to nonzero TMR with periodic oscillation. Studies concerning spin accumulation have also examined the magnetotransport properties for various spin relaxation times in the island because the accumulation occurs when the spin of an electron entering a particle does not flip until the next electron arrives.

On the other hand, in the case of the cotunneling process [38], magnetotransport phenomena have been analyzed in a Coulomb blockade region [36, 39-41]. In contrast to those in sequential tunneling, which occur outside of a Coulomb blockade regime and with in the limit of high tunnel resistance, cotunneling gives a dominant contribution when the tunnel resistances are no more than 1 or 2 orders higher than the resistance quantum. Assuming a double junction, the total tunnel resistance for sequential tunneling is proportional to the sum of the resistances, while that for cotunneling is proportional to their product. It has been predicted that this discrepancy would lead to enhanced TMR in a cotunneling regime [41].

Experimentally, there have been several studies [42-72]. The first experimental evidence for characteristic SD-SET phenomena was observed by Ono et al. in 1995 [42]. They fabricated Ni / NiO / Co / NiO / Co double junctions with small contact area ($\sim$200nm^2) and measured magnetotransport properties by changing the gate voltage at a low temperature, below 1 K. In the Coulomb blockade region, they found enhanced TMR exceededing 40 % in the off-state but only reacing 4 % in the on-state. The enhancement was theoretically explained by a strong tunneling model in which the tunnel resistances were near the resistance quantum [39, 73]. Although the authors of these studies successfully observed enhanced TMR, the operating temperature was lower than 100 mK because the size of the microfabricated island was larger than 100 nm. Schelp et al also found a Coulomb blockade effect on TMR in a sample with nanometric Co clusters [55]. They prepared a layered Co / Al-O / Co clusters / Al-O / Co sample and observed twice-larger TMR at 4.2 K than that at RT. The origin for enhanced TMR was suggested to be the effect from the Coulomb blockade in Co clusters. Their observation of the Coulomb blockade and TMR even in the sample with a very large contact area was of significance, because they showed the potential of studying SD-SET in a layered structure. Following their study, several other SD-SET studies in layered structures have been performed [48, 53, 56, 58, 63, 65]. In order to understand the mechanism of SD-SET, as mentioned above, it is necessary to divide the properties of SD-SET into two categories according to transport mechanisms: cotunneling and sequential tunneling. Although there have been some reports on enhanced TMR ascribed to finite spin-dependent transport due to the cotunneling process, no experimental evidence in a sequential tunneling regime has been reported. We

have fabricated appropriate sample structures using Co-Al-O insulating granular films, and elucidated SD-SET phenomena in sequential tunneling [60, 63-65] and co-tunneling regimes [62, 66] individually. Our study is the first to reveal an oscillatory TMR behavior in a sequential tunneling regime. The details are described later.

2.3 Spin accumulation in nanoparticles

Spin injection and accumulation were first studied in a layered sample where a normal metal (NM) layer was sandwiched between two ferromagnetic (FM) layers. A non-equilibrium effect of spin accumulation is generated by a spin-polarized current from one FM layer into the NM layer. When the NM layer is thinner than the spin-diffusion length, a spin injection signal attributed to spin accumulation in the NM layer is detected in the other FM layer according to the relative orientation of the two FM layers [74]. Spin accumulation has also been studied in sub-micrometer-sized lateral structures [75, 76]. In this manuscript, we discuss the spin accumulation effect in an isolated nanoparticle in which spin-polarized current is injected through a tunnel barrier. In such a system, spin accumulation in the nanoparticle occurs when the spin relaxation time overcomes the interval of successive electron tunneling [15, 19, 21, 23, 25, 36, 37, 77, 78]. According to the sample structure shown in the Ch. 6, we introduce the FM / I / FM nanoparticle / I / NM model (I: insulating barrier) as illustrated in Fig. 2-3. As mentioned in Ch. 2, Sec.1, a tunnel conductance G_σ for a spin states σgs expressed by the multiplication of the initial and final density of states (DOS) of the σ spin band at Fermi level (E_F). There should be a discrepancy between incoming and outgoing numbers of spins at a fixed spin state because the DOS at E_F of FM is spin-polarized while that of NM is not. This gives rise to the increase (or decrease) of spin population leading to the shift of the chemical potential ΔE_F^σ for a σ spin state. In order to maintain charge neutrality in the particle, the chemical potential of another σ shifts in the opposite direction, satisfying $D_\uparrow \Delta E_F^\uparrow = -D_\downarrow \Delta E_F^\downarrow$. Although the degree of the shift depends on the net DOS of the particle, $\Delta E_F^\uparrow$is not the same as $\Delta E_F^\downarrow$ because the net DOS is spin-polarized around E_F. In order to maintain spin-conservation conditions, the following expression is applied:

$$\frac{(I_{1,\sigma} - I_{2,\sigma})}{e} = \frac{D_\sigma \Omega}{\tau_{SF}} \Delta E_F^\sigma \tag{2.11}$$

where $I_{i,\sigma}$ is the current at the i^{th} junction (i= 1, 2) for spin σ, Ω is the volume of the particle, τ_{SF} is the mean spin relaxation time in a nanoparticle defined as $\tau_{SF}^{-1} = (\tau_\uparrow^{-1} + \tau_\downarrow^{-1})/2$, and τ_σ is the spin relaxation time of electrons with spin σ. When we consider the spin accumulation effect in SET regime, the bias-voltage dependence of ΔE_F^σshows a sawlike oscillation with a period close to that of the Coulomb staircase. In the case of the Co nanoparticle, characteristic oscillation gives rise to modifications in the current – bias voltage curve resulting in novel TMR behavior. Details will be shown in Ch. 6.

3. Insulating granular film

3.1 Materials, sample preparation and microstructure

Insulating granular films consist of small metallic particles and an insulating matrix. If the composition of the metal is lower than the percolation limit, the transport is dominated by the tunneling of electrons between particles. If the particles are magnetic, TMR arises because the magnetization vectors on particles, which are not aligned at low applied fields, become more aligned as the applied field increases, leading to a decrease in resistivity. Pioneering works on TMR in insulating granular films were published by Gittleman et al. .[79] and by Helman and Abeles [80], both of whom used Ni-Si-O films. However, the magnitudes of TMR were very small. In 1994 Fujimori et al. used a Co-Al-O granular film and reported a large TMR, which reached 10 % even at rooom temperature [81]. This ratio was found to increase with decreasing temperature, exceeding 20 % at low temperatures [62, 82].

Insulating granular films are easily prepared by sputtering and evaporation techniques. As shown in Fig. 3-1, the primary methods we used included (a) reactive sputtering, (b) sputtering with a composition target, and (c) tandem deposition with plural targets. We show the details of these methods for the preparation of a Co-Al-O granular film. In the case of (a), a Co-Al alloy target was sputtered in an $Ar+O_2$ atmosphere; then Al was selectively oxidized. In the case of (b), Al_2O_3 sheets are were placed over a Co target, and sputtering was performed in an Ar atmosphere. In the case of (c), there were two cathodes with targets, Co and Al_2O_3, and the rotation of the substrate holder caused the alternation of their deposition. In all cases, a granular structure comprising nanometer-sized Co metal particles embedded in an insulating Al-O matrix is formed on substrates.

In this manuscript, we employed Co-Al-O films prepared by the reactive sputtering method. Hereafter the Co-Al-O granular film containing x at.% Co, y at% Al and z at.% O is denoted $Co_xAl_yO_z$. The compositions are determined by Rutherford backscattering spectroscopy (RBS) analysis. The atomic composition of Co was roughly controlled by that in the Co-Al target. On the other hand, the composition of the film, at its fixed target composition, is relatively insensitive to the oxygen gas flow ratio. For example, in the case of the $Co_{36}Al_{22}O_{42}$ film, the target composition was fixed to be $Co_{25}Al_{75}$ while the oxygen gas flow ratio was allowed to range from 1.6 % to 3.0 % (at total gas pressure $\sim$ 1mTorr).

Figs. 3-2 show (a) plan view and (b) cross-sectional transmission electron microscopy (TEM) micrographs for $Co_{46}Al_{19}O_{35}$ film [83]. The film has an isotropic granular structure consisting of Co particles 2-3 nm in diameter (dark spheres) and intergranular Al-O about 1 nm in thickness (white channels). Fig. 3-3 shows a high resolution TEM micrograph for $Co_{52}Al_{20}O_{28}$ film, indicating that a crystalline Co particle is surrounded with non-stoichiometric aluminum oxide with amorphous structure.

3.2 Electric transport and magnetic properties in insulating granular systems

As mentioned above, the electric charging effect of small islands causes a Coulomb blockade when the charging energy overcomes the thermal and/or bias potentials. An insulating granular system consists of metallic nanoparticles embedded in an insulating matrix. Each nanoparticle is electrically isolated; their average size is a few nanometers while their charging energy exceeds 100 K. The electric transport in insulating granular systems represents a characteristic dependence on temperature. Fig.3-4 shows the temperature dependence of electrical resistivitygρ for Co-Al-O films of different compositions: $Co_{54}Al_{21}O_{25}$, $Co_{52}Al_{20}O_{28}$, $Co_{46}Al_{19}O_{35}$, and $Co_{36}Al_{22}O_{42}$. The plot of ln ρ versus $T^{-1/2}$ is approximately linear for all the films. The relationship of $\ln\rho \propto 1/\sqrt{T}$was first derived by Sheng *et al.* [84], considering electron tunneling, charging effect and particle size distribution. They analyzed its temperature dependence assuming a model in which particles on each contribution path have the same size d and are separated by a barrier thickness s, keeping their ratio s/d (or equivalently $E_c s$) constant for a given composition. In this model, the electrical conductivity is dominated by tunneling between small particles at high temperature and between large ones at low temperatures because larger ones cause a Coulomb blockade as the temperature decrases.

For a conventional sandwich-type tunnel junction, the tunnel conductance is temperature independent and proportional to exp{- $2(2\pi/h)(2m\phi)^{1/2}s$}, where h is the Planck's constant, m the effective electron mass, ϕ the effective barrier height, and s the barrier width. In the case of an insulating granular system, the existence of finite charging energy (E_c) gives rise to the particular temperature dependence of ρ. The number density of the charge carrier, whose generation requires an E_c, is proportional to the Boltzmann factor $\exp\{E_c/2k_BT\}$, where E_c is the Coulomb energy, k_B the Boltzmann's constant, and T the absolute temperature. The final formula about ρ was obtained as

$$\rho \quad = \quad \rho_0\{\exp\{2(C/k_B)^{1/2}T^{-1/2}\}, \tag{3.1}$$

where $C = (2\pi/h)(2m\phi)^{1/2}\ sE_c$ which was named the tunnel activation energy. Eq. (3-1) can be transformed to

$$\ln\rho = 2(C/k_B)^{1/2}T^{-1/2} + const. \tag{3.2}$$

The linear relation found experimentally in Fig. 3-4 agrees with Eq. (3-2). From the gradient of the log ρ versus $T^{-1/2}$, C is estimated to be 30 meV for the $Co_{36}Al_{22}O_{42}$film.

Figs. 3-5 (a) and (b) show $M-H$ and $M-T$ curves, respectively, for the $Co_{36}Al_{22}O_{42}$ film. The M-H curves at RT show no remanence at zero field and unsaturated behavior in high fields. Large thermal hysteresis is observed between zero-field cool (ZFC) and field cool (FC) curves, and it is suggested that particles are superparamagnetic at room temperature and that thermal fluctuation of the magnetic moments is blocked at 4.5 K. Figs. 3-6 (a) and (b) show

MR curves for $Co_{36}Al_{22}O_{42}$ measured at RT and 4.2 K, respectively. Large values of MR exceeding 10 % are observed. At RT MR does not completely saturate even at 80 kOe; on the other hand, MR nearly saturates above 20 kOe at 4.2 K. The coercivity and hysteresis of the MR curve appearing at 4.2 K corresponds to the magnetization curve shown in Fig. 3-5 (a).

3.3 Particle size distribution in insulating granular systems

The sizes of nanoparticles in insulating granular films are distributed; information on the particle size distribution is essential to understanding the mechanism of TMR phenomena [85]. Ohnuma et al. [83, 86] reported the microstrustures in Co-Al-O granular films investigated by high-resolution transmission electron microscopy (HRTEM) to obtain the distributions of particle sizes and interparticle distances. We have evaluated particle size distributions in $Co_{36}Al_{22}O_{42}$ granular films by fitting the magnetization curves to the Langevin function which describes superparamagnetic behavior.

Magnetization in the superparamagnetic state can be described by the Langevin function. If we assume that all the Co particles have a spherical body with the same diameter d and if the anisotropy energy is negligible, the magnetization M is described by

$$\frac{M}{M_s} = L(\alpha) = \coth\alpha - \frac{1}{\alpha} \tag{3.3}$$

with

$$\alpha = \frac{\mu H}{k_B T} = \frac{M_{Co} H}{k_B T} \frac{4\pi}{3} \left(\frac{d}{2}\right)^3 \quad , \tag{3.4}$$

where Ms is the saturation magnetization of the sample, MCo is the magnetization of Co particles and H is the applied field. In real systems, d has a distribution; we use a log-normal distribution function (LNDF) in d. LNDF is described by

$$f(d) = \frac{1}{\sqrt{2\pi}\ln\sigma} \exp\left[-\frac{(\ln d - \ln d_m)^2}{2\ln^2\sigma}\right] \quad , \tag{3.5}$$

where the parameters dm and σ represent the statistical median and the geometric standard deviation, respectively. The Langevin function taking the log-normal particle size distribution into account is described by

$$M = \sum_{i=1}^{n} \left[M_{Co} \frac{4\pi}{3} \left(\frac{d_i}{2}\right)^3 f(d_i) L(\alpha_i) \right] \tag{3.6}$$

with

$$\alpha_i = \frac{M_{Co} H}{k_B T} \frac{4\pi}{3} \left(\frac{d_i}{2}\right)^3 \quad . \tag{3.7}$$

Fig. 3-7 (a) shows the calculated magnetization curves compared to the experiment for a $Co_{36}Al_{22}O_{42}$ film at $T = 200$ and 293 K; the particle size distribution

which gives the best fit is shown in Fig. 3-7 (b). The sizes of particles are distributed mostly in the range of 1.0 to 5.0 nm in diameter and $d$mag is estimated to be 2.45 nm. This $d$mag is consistent with that evaluated from the TEM image d_{TEM} (= 2.20 nm).

4. Spin-dependent higher order tunneling in Coulomb blockade regime

In this chapter, we report on the temperature and bias-voltage dependence of MR in insulating Co-Al-O granular films without performing microfabrication. The MR exhibits an anomalous increase at low temperatures but no significant indication of change with bias voltage. We show that the anomalous increase of the MR indicates evidence for higher-order tunneling (cotunneling) between large granules through intervening small granules [36, 62]. We emphasize that the existence of higher-order tunneling is a natural consequence of the granular structure, since a broad distribution of granule size is an intrinsic property of granular systems.

4.1 Results

Fig. 4-1 shows the temperature dependence of MR for Co-Al-O films. It is clearly seen that the MR is remarkably enhanced at low temperatures while it is nearly independent of temperature above ∼100 K. For $Co_{36}Al_{22}O_{42}$, the MR below 3 K is anomalously large and reaches more than twice the value given by $P_{Co}^2/(1+P_{Co}^2)$ [11], where the formula is half of that for magnetic tunnel junctions (MTJ) because of the difference between random and antiparallel alignment of magnetic moments. In the case of MTJ with an Al-O barrier, the temperature dependence of MR is discussed on the basis of magnetic impurity or magnon scattering. However, it is considered that magnetic impurity or magnon scattering does not give rise to the plateau in the temperature dependence of MR, as in the present result observed above ∼100 K. Helman and Abeles [80] proposed a theory of spin-dependent tunneling in insulating granular systems and predicted the temperature dependence $1/T$ for MR. However, the dependence $1/T$ does not fit the present results.

Transport properties were measured in the current-perpendicular-to-plane (CPP) geometry as shown in Figs. 4-2 where a 1-μm-thick $Co_{36}Al_{22}O_{42}$ granular film was sandwiched between upper and lower Au-Cr electrodes. Figs. 4-3 (a) and (b) show ρ and MR at 4.2 K, respectively, as functions of bias voltage V_b for a $Co_{36}Al_{22}O_{42}$ film. ρ decreased rapidly by 3 orders of magnitude as the bias voltage increased from $V_b = 0$ up to 600 mV. Nevertheless, the magnitude of the enhanced MR was almost constant. This is in clear contrast with the case of MTJ of macroscopic size, where both MR and ρ decrease gradually with increasing bias voltage. Furthermore, the bias-voltage dependence of MR is much smaller than the temperature dependence of MR in Fig. 4-1. We can consider that about 200–300 Co granules exist in the direction normal to the film plane between the upper and the lower electrodes, assuming an average particle size $\langle d \rangle$ of 2.5 nm and interparticle distance $\langle s \rangle$ of 1 nm. Therefore, the applied bias voltage per one microjunction consisting of two neighboring Co granules may be estimated to be 2–3 mV at $V_b = 600$ mV, which corresponds to 20–30 K in temperature. As seen in Fig. 4-1, the enhanced MR decreases rapidly with increasing temperature and becomes flat around 20–30 K, while it

is independent of V_b at least up to 600 mV (2-3 mV at neighboring ones).

4.2 Theoretical explanation

In granular systems with a broad distribution in particle size [85], it is highly probable that large particles are well separated from each other due to their low number density (i.e., the larger the granule size, the more separated the granules), and there may be a number of smaller granules between large granules as shown in Fig. 4-4 (a). To model the structural feature of granular systems we assume that large granules with size $n\langle d\rangle$ and charging energy $\langle E_c\rangle/n$ are separated by an array of n particles with average size

$$\langle d\rangle$$

and charging energy $\langle E_c\rangle$ on a conduction path, as shown in Fig. 4-4 (b).

4.2.1 Temperature dependence of MR

We first calculate the temperature dependence of the conductivity $\sigma(T)$ at zero-bias voltage ($V_b = 0$). The tunnel current at the zero-bias limit is dominated by thermally activated charge carriers. In the case of the conduction path in Fig. 4(b), the carriers mostly occupy the large particle of charging energy $\langle E_c\rangle/n$ in a probability proportional to the Boltzmann factor $\exp[-\langle E_c\rangle/2nT]$ in units of $k_B = 1$. Since the large particles are separated by the smaller ones, the ordinary tunneling of an electron from a large particle to a small one increases the charging energy by $\delta E_c \sim {}^1\!/_2 \langle E_c\rangle/(1+1/n)$; thus is suppressed by the Coulomb blockade at low temperatures $T < \delta E_c$. In this regime, the dominant contribution to$\sigma(T)$ comes from higher-order processes of spin-dependent tunneling where the carrier is transferred from the charged large particle to the neighboring neutral large particle through an array of small particles, using successive tunneling of single electrons, i.e., the cotunneling of (n+1) electrons. Figure 4-4 (a) shows an example of the third-order process (n=2). Summing up all of these higher-order processes, we have

$$\sigma(T) \propto \sum_n e^{-\langle E_c\rangle/2nT}[(1+P^2m^2)e^{-2\kappa s'}]^{n+1}\left(\frac{(\pi T)^2}{(\delta E_c)^2+\gamma^2(T)}\right)^n f(n) \quad (4.1)$$

Here, [—] is the spin-dependent tunneling probability between the neighboring particles, $m = M/M_s$ is the magnetization normalized to the saturation magnetization M_s, κ is the tunneling parameter related to the barrier height, and $s' = 2n\langle s\rangle/(n+1)$ with $\langle s\rangle$ being the mean separation of particles with size$\langle d\rangle$. The factor $(—)^n$ represents the finite temperature effect by which electrons (or holes) in the energy interval of πT around the Fermi level participate in the intermediate states of the higher-order process [87], and $\gamma(T)$ is the decay rate given by $\gamma(T) \approx gT$ with g being a constant .[88]. The function $f(n)$ represents the distribution of the conduction paths. In Eq. (4.1), $\exp[4\tilde{\kappa}n\langle s\rangle - \langle E_c\rangle/2nT]$ is a peaked function of n and has its maximum at $n* = (\langle E_c\rangle/8\tilde{\kappa}\langle s\rangle T)^{1/2}$, where

$\tilde{\kappa}/\kappa \approx 1 + (1/4\kappa \langle s \rangle) \ln \left[(g/\pi)^2 + (\langle E_c \rangle / 2\pi T)^2 \right]$. The existence of higher-order tunneling processes with different orders is a natural consequence of the granular structure since a broad distribution of granule sizes is an intrinsic property of granular systems. Namely, cotunneling processes with $n = 1$ occur in some places, while those with $n = 2$ occur in other places, thus n (and consequently n^*) can be treated as a continuous variable at low temperatures ($T << \langle E_c \rangle$). Replacing the summation by the integration in Eq. (4.1) and using the method of steepest descent [89], we obtain

$$\sigma(T) \propto \left(1 + P^2 m^2\right)^{n*+1} \sqrt{\frac{n*}{\tilde{\kappa} \langle s \rangle}} f(n*) \exp \left[-2 \sqrt{\frac{2\tilde{\kappa} \langle s \rangle \langle E_c \rangle}{T}} \right] \quad . \tag{4.2}$$

In Fig. 4-5, the calculated resistivity for $m = 0$ is shown by the solid lines. Here and hereafter, we assume $f(n*) \propto 1/n*$, and take $2\kappa \langle s \rangle = 3$, g = 0.3, and the values of $\langle E_c \rangle$ are estimated to be 9 K for $Co_{54}Al_{21}O_{25}$, 18 K for $Co_{52}Al_{20}O_{28}$, 25 K for $Co_{46}Al_{19}O_{35}$, and 110 K for $Co_{36}Al_{22}O_{42}$.

Because of the higher-order processes, the spin-dependent part of $\sigma(T)$ in Eq. (4.2) is amplified to the $(n^* + 1)$th power of $(1 + P^2 m^2)$, so that $\sigma(T)$ is sensitive to the applied magnetic field since m varies from $m = 0$ to $m = 1$ (the fully magnetized state) by application of the magnetic field. Using Eq. (2) the MR, $\Delta\rho/\rho_0 = 1 - [\sigma(T)]_{m=0} / \sigma(T)$, is expressed as

$$\frac{\Delta\rho}{\rho_0} = 1 - \left(1 + m^2 P^2\right)^{-(n*+1)} . \tag{4.3}$$

The calculated MR is shown by the solid curves in Fig. 4-1, where the value of P is chosen to fit the experimental data. For small P^2, Eq. (3) is approximated to be

$$\frac{\Delta\rho}{\rho_0} = P^2 m^2 \left(1 + \sqrt{\frac{C}{T}}\right) \tag{4.4}$$

with $C = \langle E_c \rangle / 8\tilde{\kappa} \langle s \rangle$ being constant. Eq. (4.4) indicates an anomalous increase of $\Delta\rho/\rho_0$ at low temperatures due to the onset of higher-order processes between larger granules, i.e., $n* \propto 1/\sqrt{T}$. At $T = 2$ K, n^* takes the value of 1.6, so that one or two small granules intervene between larger ones in the higher-order processes. As seen in curve a, the MR grows rapidly around 10 K well below $E_c = 110$ K. Similar behavior is seen in a double-junction system [41] [36].

4.2.2 Bias voltage dependence of MR

We next calculate the bias-voltage dependence of conductivity $\sigma(V_b)$ in the Coulomb blockade regime. When a finite voltage V_b is applied to the granular system, the voltage drop ΔV_b between the large granules in the model system of Fig. 4-4 (b) is given by $\Delta V_b = (2n/N_g) V_b$, where N_g is the average number of glanules along a conduction path. $\sigma(V_b)$ at finite temperatures, the factor $(\pi T)^{2n}$ in Eq. (4.1), is replaced by $\left[(\pi T)^2 + (2eV_b/N_g)^2 \right]^n$ [87]. We obtain

$$\sigma(V_b) \propto \sum_n e^{-\langle E_c \rangle / 2nT} [(1 + P^2 m^2) e^{-2\kappa s'}]^{n+1} \left[1 + \left(\frac{2eV_b}{N_g \pi T} \right)^2 \right]^n f(n) . \tag{4.5}$$

Following the same procedure as in deriving $\sigma(T)$ in Eq. (4.2), we obtain the bias –dependence of the conductivity

$$\sigma\left(V_b\right) = \sigma\left(T\right)\left[1 + \left(\frac{2eV_b}{N_g \pi T}\right)^2\right]^{n*} . \tag{4.6}$$

The $\sigma(V_b)$ exhibits a power low dependence $(1/V_b)^{2n*}$ for $T \quad < eV_b/N_g$.

In Fig. 4-2 (a), we show the calculated resistivity $\rho_0\left(V_b\right) = 1/\sigma\left(V_b\right)$ by the solid curves for $T = 4.2$ K and $N_g = 140$. The steep decrease of the calculated resistivity is in good agreement with that of the experimental data. In Fig. 4-3 (b), the calculated MR is shown by the solid curve. The enhanced MR is maintained upon application of higher voltages, which is consistent with the experimental result. The constant MR may originate from the large number of granules along the conduction paths in the granular films, in which the voltage drop between neighboring granules $\sim V/N_g$ is small for a large value of N_g. V / N_g at $V_b = 500$ mV is about 3 mV for $N_g = 140$ and its corresponding temperature is ~ 40 K, which is smaller than that of the charging energy $\langle E_c \rangle \quad \sim 110$ K. We note that the enhanced MR is nearly constant up to 500 meV, whereas the corresponding resistance is reduced by several orders of magnitude. This is in contrast with ferromagnetic tunnel junctions of macroscopic size, where both the MR and the resistance decrease gradually with increasing bias voltage.

5. Spin-dependent single-electron tunneling in microfabricated structures

5.1 Current path restriction to observe spin-dependent single-electron tunneling in sequential tunneling regime

Insulating granular films consisting of nanometer-sized magnetic metallic particles embedded in an insulating matrix are useful for the study of spin-dependent SET (SD-SET) phenomena. The properties of SD-SET are roughly divided into two categories according to transport mechanisms: cotunneling and sequential tunneling. In the last chapter, we discussed one characteristic SD-SET behavior due to cotunneling in the Coulomb blockade regime. Here we discuss about the SD-SET behaviors in a sequential tunneling regime: in other words, TMR behaviors associated with a Coulomb staircase and/or clear Coulomb threshold, in microfabricated samples.

In granular film of a macroscopic size containing a large number of particles, however, SET phenomena, represented by Coulomb staircase and so on, are averaged out due to the large distributions of particle sizes and interparticle distances [62, 83, 85]. The tunnel paths should be restricted in order to clearly observe the SET phenomena. A simple method to restrict the tunnel paths is to use scanning tunneling microscopy (STM). The tunnel path on the surface is limited to only one particle just below the STM tip. We observed clear Coulomb staircases in the $I - V_b$ measurements for Co-Al-O granular films even at room temperature [90, 91]. Figs. 5-1 (a) and (b) show typical examples of an STM topographic image and an $I - V_b$ curve, respectively, for a $Co_{36}Al_{22}O_{42}$ film.

A more advantageous method than STM for a variety of measurements and applications is to fabricate a device structure consisting of a small part of granular film with nanofabricated electrodes. In this study we have fabricated two types of device structures with Co-Al-O granular films using focused ion-beam (FIB) milling or electron-beam lithography techniques. One is a granular nanobridge structure [60, 67]: point-shaped electrodes separated by a very narrow lateral gap filled with Co-Al-O granular film. The other is a current-perpendicular-to-plane (CPP) geometry structure [63-65]: a thin Co-Al-O granular film sandwiched by ferromagnetic electrodes with the current flowing in the direction perpendicular to the film plane through a few Co particles. We measured the $I - V_b$ curves in these samples, and found the enhancement and oscillation of TMR due to spin-dependent SET in a sequential tunneling regime.

5.2 Results in nanobridge structures

5.2.1 Experimental procedures and results

In this section, we report enhanced TMR just above the Coulomb blockade threshold in a sequential tunneling regime [60]. We fabricated point-shaped electrodes separated by a very narrow lateral gap filled with insulating granular film; we call the resulting structures "granular nanobridges". As mentioned in the last section, the mechanism for TMR enhancement is different from that

for higher-order tunneling, because this enhancement in nanobridge samples is caused outside the Coulomb blockade regime. We apply the orthodox theory of SET [9] and explain that enhanced TMR is brought about by the modification of the detailed balance of particle charges by the external magnetic field [14, 16, 91].

A schematic view of a typical sample is shown in Fig. 5-2 (a). An insulating granular nanobridge was fabricated on a Corning no. 7059 glass substrate as follows: a 15 nm-thick-NbZrSi amorphous layer was deposited by rf sputtering, and was formed into source and drain electrodes by FIB etching using 30 kV gallium ions (Seiko Instruments Inc., SMI 9200). The electrodes separated by a gap with a length (l), i.e., gap separation, of 30 nm and a width (w) of 60 nm are shown in Fig. 5-2 (b). Deep trenches (60 nm wide and 200 nm deep) were formed beside the gap by FIB etching to avoid the formation of unnecessary current paths outside the gap. A 7.5-nm-thick Co-Al-O granular film was deposited on the patterned surface by reactive rf sputtering, and the gap was filled by the Co-Al-O film. The aspect ratio of trenches was so high that the trenches were not filled with the Co-Al-O film. The composition of Co-Al-O was determined to be $Co_{36}Al_{22}O_{42}$ by RBS analysis. The average size of Co particles was estimated to be about 2.5 nm from the analysis of the superparamagnetic behavior and TEM observation [85]. The characteristic sizes of granular nanobridges, i.e., w, l, and thickness (t), varied in the range of 60 - 700 nm, 30 - 70 nm and 5 - 30 nm, respectively. $I - V_b$ characteristics were measured at 4.2 K using an electrometer (Keithley 6514) with a two-terminal arrangement. TMR ($= \Delta R/R_{max}$) was evaluated from the difference between the $I - V_b$ curves at the applied field $H = 0$ and 10 kOe.

Fig. 5-3 (a) shows the $I - V_b$ curves at H=0 (solid lines) and H=10 kOe (dashed lines) for the sample with w=60 nm, l=30 nm and t=7.5 nm. Here, the threshold voltage V_{th} was defined as that below which the current was zero within an accuracy of 100 fA, and it was approximately 1.5 V in this case. In the range of $|V_b| < V_{th}$, a Coulomb blockade occurred, and the current increased rapidly when $|V_b|$ exceeded V_{th}. It is noted that for Co-Al-O granular films of macroscopic sizes, the Coulomb blockade has not clearly been observed, because the macroscopic sample contains a lot of Co particles with a broad distribution of sizes and the tunneling of electrons between large particles with small E_c could start at small voltages. In the granular nanobridge, however, the tunnel paths are so limited that the Coulomb blockade is remarkable.

Fig. 5-3 (b) shows the V_b dependence of TMR. TMR depends strongly on V_b. For $|V_b|$ <4.0 V, TMR increases with decreasing $|V_b|$ and reaches a maximum value larger than 30 % at the voltage slightly above V_{th} ($\sim$1.5 V). In the Coulomb blockade region, *i.e.*, $|V_b| < V_{th}$ (hatching area), there is little quantitative reliability of the measurements because the current is very low (<100 fA). For $|V_b| > 4.0$ V, on the other hand, TMR is about 8 % showing no large change with V_b, although weak oscillatory behavior seems to exist in the V_b dependence of TMR.

Similar results have been obtained in other granular nanobridges of different sizes. Figs. 5-4 (a) and (b) show the $I - V_b$ curve and the V_b dependence of

TMR, respectively, for the sample with w=700 nm, l=40 nm and t=15 nm. V_{th} is observed to be 0.5 V, which is lower than that in the sample shown in Fig. 5-3. V_{th} shows a tendency to increase as the size of the granular nanobridge decreases. The voltage where the TMR shows a maximum, V_p, is slightly larger than V_{th}. Fig. 5-5 shows V_p vs. V_{th} in granular nanobridges of different sizes. A clear correlation between V_p and V_{th} is seen, suggesting that the enhanced TMR is caused by the Coulomb blockade.

5.2.2 Theoretical explanation

The orthodox theory of SET [9] can be used to explain the experimental results, particularly the enhanced TMR near V_{th}. In the orthodox theory, the tunnel path is modeled as an equivalent classical electrical circuit. For the granular nanobridge, we assume a parallel circuit of triple tunnel junctions as shown in Fig. 5-6 (a). This is the simplest model to explain our experimental results because we need at least two magnetic particles in each series of junctions to study the spin-dependent transport in nanobridges with nonmagnetic electrodes. We neglect the higher-order tunneling process, i.e., cotunneling [41, 62], because the tunnel resistances between particles and between an electrode and a particle are estimated to be about 10^5 times larger than $R_Q \approx$25.8 kΩ. In order to obtain a stable tunneling current, we constructed a detailed balance equation for the probability of states $p(\{n_i\}_\alpha)$, which is given in the matrix form by

$$\dot{p} = \mathbf{M}p = 0, \tag{5.1}$$

where $p = (\ldots, p(\{n_i\}_\alpha), \ldots)^T$, and $\mathbf{M}$ is the transition matrix in the configuration space constructed by $\{n_i\}_\alpha$ with the index α labeling the different charge states. The tunneling current through the k^{th} junction is given by

$$I_k = e \sum\nolimits_\alpha p(\{n_i\}_\alpha) \left[\Gamma_k^+(\{n_i\}_\alpha) - \Gamma_k^-(\{n_i\}_\alpha)\right], \tag{5.2}$$

where $\Gamma_k^{+(-)}(\{n_i\}_\alpha) \propto 1/R_k$ is the forward (backward) tunneling rate through the k^{th} junction with the initial charge state $\{n_i\}_\alpha$. Current conservation requires that the tunneling current I_k is the same for all the junctions in each series. Let us evaluate the tunneling current at the junction between a nonmagnetic electrode and a particle, where the tunneling rate $\Gamma_k^{+(-)}(\{n_i\}_\alpha)$ is independent of the magnetic field. The magnetic field dependence of the tunneling current comes from the probability $p(\{n_i\}_\alpha)$ of the charge state $\{n_i\}_\alpha$, which is determined by Eq.(5.2). Since the transition matrix $\mathbf{M}$ contains the tunneling rates between magnetic particles, the matrix $\mathbf{M}$ and therefore the probability $p(\{n_i\}_\alpha)$ can be modified by applying the magnetic field. For V_b just above V_{th}, we have a few charge states contributing to the tunneling current, and the tunneling rates at these charge states differ greatly from each other according to thier charging energies. Therefore, the strong modification of the probability $p(\{n_i\}_\alpha)$ is made to satisfy the detailed balance equation, and the TMR is strongly enhanced just above V_{th}. This kind of TMR enhancement in double tunnel junctions has been studied by Barnas and Fert [14] and by Majumdar

and Hershfield [16]. They also predicted the oscillating behavior of TMR against V_b associated with the Coulomb staircase. No Coulomb staircase appears in the $I-V_b$ curves of granular nanobridges; however, a small-magnitude oscillation of TMR could be observed (see Figs. 5-3 and 5-4). There is no strong asymmetry in tunnel resistances, i.e., no bottleneck in tunnel paths of granular nanobridges, leading to no Coulomb staircase and only weak oscillation of TMR. Moreover, we have many junction arrays in a granular nanobridge, and the randomness of junction capacitances also muddies the TMR oscillation.

In order to explain the experimental results for the sample with w=60 nm, l=30 nm and t=7.5 nm (Fig. 5-3), we considered a parallel circuit of 20 triple tunnel junctions and assumed that the tunnel resistance between an electrode and a particle is expressed as $R_{ep} = (1 \pm \delta)\overline{R}_{ep}$, where δ is the deviation from the typical value $\overline{R}_{ep}$. Other junction parameters such as tunnel resistances between particles R_{pp}, junction capacitances C_{ep}, and C_{pp} were also assumed to be distributed around the mean values, *i.e.*, $R_{pp} = (1 \pm \delta)\overline{R}_{pp}$, $C_{ep} = (1 \pm \delta)\overline{C}_{ep}$, and $C_{pp} = (1 \pm \delta)\overline{C}_{pp}$. The deviation δ for each junction parameter was randomly chosen within the range of -0.1<δ<0.1. The temperature was set to be 4.2 K and the typical value of tunnel resistances for the parallel alignment of magnetizations was taken to be

$$\overline{R}_{pp} = \overline{R}_{ep}/2. \tag{5.3}$$

The tunnel resistance between particles for the antiparallel alignment of magnetizations was larger than that for the parallel alignment and is expressed using the spin polarization P as

$$\overline{R}_{pp} = (\overline{R}_{ep}/2) \cdot (1 + P^2)/(1 - P^2), \tag{5.4}$$

where P is assumed to be 0.42 for Co [92]. The typical values of junction capacitances are taken to be $\overline{C}_{ep} = 0.1aF$ and $\overline{C}_{pp} = 0.05aF$, which are reasonable values considering the average particle size and interparticle distance in Co-Al-O granular films [83, 85].

The V_b dependence of TMR obtained by the numerical calculation is shown in Fig. 5-6 (b). One can see that the theoretical result is in good agreement with the experimental one. The TMR is enhanced just above V_{th} ($\sim$1.5 V) and decreases with V_b. The randomness of junction capacitances obscures the oscillation of the total TMR as shown in Fig. 5-6 (b). We may consider that the quantitative difference between V_{th} and V_p is not essential, but it is caused by effects such as the leakage of current through the glass substrate.

5.3 Results in CPP geometry structures

In the last section, we fabricated nanobridge structures for combining insulating granular films with microfabricated electrodes and successfully found enhanced TMR at the Coulomb threshold voltage. Proper limitation of the number of current paths made it possible to observe spin-dependent SET. However, no Coulomb staircase was observed. In an assembly of nanoparticles such

as granular films, the Coulomb staircase is expected to appear when the tunnel resistance between two neighboring particles or between a particle and an electrode is much larger than the other resistances in the current path. In other words, a bottleneck of tunnel conductance must exist somewhere in the current path [9, 36]. In this section, in order to investigate the relationship between the Coulomb staircase and TMR, we employed CPP (Current-Perpendicular-to-Plane) geometry measurements in Co-Al-O granular films. A bottlenech is easily added to samples for CPP geometry measurements for the sake of observing Coulomb staircases. We prepared CPP geometry samples, where a thin Co-Al-O granular film was sandwiched by ferromagnetic electrodes and a very thin Al-O layer was inserted between the bottom electrode and Co-Al-O as a bottleneck, and measured the current (I) – bias voltage (V_b) characteristics. We succeeded in observing clear Coulomb staircases due to the current confinement among the vast number of channels between the upper and lower electrodes [65].

We fabricated CPP geometry samples by a focused ion-beam (FIB) etching process. Fig. 5-7 (a) represents a schematic illustration of a sample. Samples were prepared on Si/SiO_2 substrates by rf sputtering. A bottom electrode was first deposited, and then a thick Al-O film (40 nm) was deposited onto the bottom electrode as an insulating layer using an Al_2O_3 target. Next, a small contact area was made by FIB milling (Fig. 5-7 (b)). A contact area of about 0.5 x 0.5 μm^2 was estimated from the scanning ion microscopy image. The milling process was carefully performed to leave a very thin Al-O layer, which contributes to forming a bottleneck. After making the contact window, furthermore, a 1$\sim$2 nm thick Al-O layer was deposited. Consequently, the bottleneck is given by the combination of the residual Al-O and the deposited Al-O layer. A 7$\sim$12 nm-thick Co-Al-O granular layer followed by a top electrode was finally deposited. The deposition of Co-Al-O granular films was done through the use of reactive sputtering in a mixture of $Ar+O_2$ atmosphere. $I - V_b$ characteristics were measured at 4.2 K using an electrometer (Keithley 6514) with a two-terminal arrangement. TMR ($= \Delta R/R_{max}$) was evaluated from the difference between the $I - V_b$ curves at the applied field $H = 0$ and 10 kOe. The external magnetic field was usually applied in the direction parallel to the plane.

Fig. 5-8 (a) shows $I - V_b$ curves at $H = 0$ (solid lines) and $H = 10$ kOe (dashed lines) at 4.2 K. Clear Coulomb staircases are observed for both $I - V_b$ curves. The first three steps from zero bias appear every 20 mV; however, the steps at higher bias voltages do not maintain a regular period. In spite of more than 10^4 parallel current paths between the electrodes in the contact area (0.5 x 0.5 μm^2), which is much larger than the average Co particle size (2.5 nm), clear Coulomb staircases were observed. This suggests that the current at low bias voltages preferentially flow along certain restricted local paths where the total charging energy determined from the sum of capacitances through the path is the lowest. Similar results were previously reported in CPP measurements for nonmagnetic granular films [93]. It is considered that at higher voltages the contribution of various current paths including those with higher charging energy appears to lead to the irregular period of Coulomb staircase.

Fig. 5-8 (b) shows the bias voltage dependence of the TMR derived from

the two $I - V_b$ curves shown in Fig. 5-8 (a). We observed the oscillation of the TMR as a function of bias voltage. The peak of TMR repeats with the period of the Coulomb staircase. The modification of the $I - V_b$ curve by the applied field seems to bring about the enhancement of the TMR with the steps of the Coulomb staircase, resulting in the oscillation of the TMR. The largest TMR (about 20 %) was seen at $V_b = 15$ mV; however, TMR converged to almost zero as the bias voltage was further increased. This is probably because the barrier quality of the Al-O bottleneck layer is still poor, leading to the rapid decrease in TMR with bias voltage. It is also noted that a sign change was observed in the TMR. One possible origin we may consider is the effect of spin accumulation. In order to clarify TMR behavior, we performed a further study considering the spin accumulation effect in a nanoparticle.

6. Spin accumulation effect in nanoparticles

We observed TMR oscillation associated with the Coulomb staircase in CPP geometry samples fabricated by FIB. In this chapter, we report experimental evidence for the spin accumulation effect in Co nanoparticles leading to the oscillation of TMR with alternate sign changes. Furthermore, the spin relaxation time in Co nanoparticles was evaluated by comparing the experimental results to numerical simulations. We discovered that the spin relaxation time in the nanoparticles is unprecedentedly enhanced up to more than the order of hundreds of nano seconds, compared to that evaluated from the spin diffusion length of ferromagnetic layers in previous CPP-GMR studies, *i.e.*,the order of tens of picoseconds.

6.1 Experimental procedures and results

In order to study this subject, the sample design and the fabrication process were modified. We fabricated pillared structures consisting of Al electrode / Al-O / Co-Al-O granular film / Co electrode layers (Fig. 6-1) to measure their magnetotransport properties in CPP geometry. Samples were prepared on thermally oxidized silicon substrates as follows: the bottom Al electrode was first deposited using ion beam sputtering (IBS), and the surface was plasma oxidized to form a conductance bottleneck layer for the observation of Coulomb staircase. A 15 nm thick Co-Al-O granular film was then deposited by reactive rf sputtering. The top Co electrode and Pt layer were deposited by IBS. This layered structure was then microfabricated to reduce the contact area using electron-beam (EB) lithography and an Ar ion etching process. An Al / Al-O / Co-Al-O / Co / Pt pillar 0.4 μm x 0.4 μm in area was prepared by the following process: EB patterning on positive resists, depositing of etching mask (Co), lift-off and Ar ion etching. To prevent short-circuiting between the electrodes, the sidewall of the pillar was then plasma-oxidized and covered with a thick Al-O also deposited by IBS. Finally a Pt layer was deposited to contact the top electrode. The sample structure is schematically shown in Fig. 6-1.

Fig. 6-2 (a) shows the $I-V$characteristics at H= 0 (black line) and H= 10 kOe (gray line) in the positive bias voltage region. The $I-V$curves reveal a definite Coulomb staircase, which was also observed in the negative bias voltage region (not shown here). The first step of the Coulomb staircase appears at about 15 mV, and the subsequent steps appear at 50 mV, 85 mV and 120 mV, respectively. We think the current preferentially flowed through a single or a few restricted local paths where only one particle was located between electrodes for the following reason: When the nominal thickness of the Co-Al-O layer was smaller than 15 nm, the samples show neither Coulomb blockade nor Coulomb staircase. In other words, 15 nm is the minimum thickness to observe the single-electron phenomena. This suggests that the Co-Al-O layer has considerable thickness fluctuation, and therefore there are some thin parts where only one particle exists in the direction normal to the film plane. (If the thickness of the Co-Al-O layer is completely uniform, three or four particles should exist in

the direction normal to the film plane everywhere, and the critical thickness for SET should be much smaller than 15 nm because the particle size is a few nm.) Furthermore, the Al-O bottleneck layer also has thickness fluctuation, playing a role as a path restriction filter. The shape of the staircase measured at $H=$ 0 is different from that of at $H=$ 10 kOe. Comparing the shapes of these two curves, it appears that the steps of the staircase at $H=0$ are steeper than those at $H=$ 10 kOe, leading to a periodic intersection of the two curves around the step points of the staircase.

Fig. 6-2 (b) shows the Vdependence of TMR derived from the $I-V$curves shown in Fig. 6-2 (a). TMR oscillates with the same period as the staircase, ranges from -10 % to +15 % and shows alternate sign changes: negative peaks, *i.e.*,inverse TMR, appear around the step points of the staircase, whereas positive bumps appear between these negative peaks. In a conventional ferromagnetic tunnel junction of macroscopic size, TMR should be limited within that expected from the spin-polarization factors of ferromagnetic components; and it decreases monotonically with bias voltage. The expected value of the TMR in this sample should be less than 2% because the resistance of the bottleneck which is located at the *spin-independent* junction between the Al electrode and a Co particle is 10 times larger than that of the other *spin-dependent* junction. Nevertheless, TMR ranging from -10 % to +15 % was observed, indicating a significant enhancement and anomalous oscillation with sign change of TMR. In order to confirm the sign of TMR, the magnetic field dependence of the electrical resistance (MR curves) was measured. Fig. 6-2 (c) shows MR curves at $V=$ 0.05 V and 0.12 V at which TMR shows negative and positive values, respectively. Both MR curves show a hysteretic behavior with two peaks according to the coercive force of the Co nanoparticles. The MR curve at $V=$ 0.05 V shows an increase of electrical resistance (R) with increasing applied magnetic field; *i.e.*,inverse TMR is observed, whereas the MR curve at $V=$ 0.12 V shows a decrease of $R$with the magnetic field. It is noted that the shift of MR curves toward the positive direction of the magnetic field is seen. A possible origin for the shift of the MR curves is the exchange bias between Co and CoO formed by the surface oxidization of the Co nanoparticles.

6.2 Numerical analysis

We performed numerical calculations on the basis of the orthodox theory with an arbitrary spin relaxation time in ferromagnetic tunnel junctions and compared it with the Vdependence of TMR in the present experiment. Since in the conducting region the Co-Al-O film contains only one nanoparticle between electrodes as mentioned before, we employed a PM / I / FM particle / I / FM double-tunnel-junction model (see Fig. 6-3 (a)) to analyze the experimental data. We considered the collinear alignment of the magnetizations. Although Fig. 6-2 (c) shows that the angle between the magnetizations of the Co particle and the Co electrode is large at zero magnetic field, it is hard to conclude that the magnetizations were aligned to be anti-parallel since the easy magnetization directions of nanoparticles were distributed randomly and the direction of

the applied magnetic field was fixed to a certain direction. If the magnetizations are non-collinearly aligned the tunneling resistance for each spin depends on the relative angle of magnetizations [11, 94] and we have to calculate the nonequilibrium spin distribution matrix [95, 96]. However, it is important to note that the calculations for collinear configurations give the lower limit of the spin relaxation time. Hereafter, we consider only the collinear configurations.

Without losing generality we can take the spin quantization axis so that the minority and majority spins of the nanoparticle are represented by $\downarrow$ and $\uparrow$, respectively. The spin accumulation occurs in the ferromagnetic island where there is a significant difference in the densities of states for minority ($D_\downarrow$) and majority ($D_\uparrow$) spins at the Fermi level due to the exchange splitting in the d-band. According to the band calculation of Co, the net spin polarization $P_{DOS} \equiv (D_\uparrow - D_\downarrow)/(D_\uparrow + D_\downarrow)$ is taken to be -0.73. In addition to P_{DOS}, another spin polarization must be taken into account, *i.e.*, that for tunneling electrons which is dominated by $s-d$hybridization [97]. It is described as P_{tun}, hereafter. $P_{tun}$of Co is assumed to be 0.35 [98]. We suppose that the energy relaxation time is so short that the Fermi distribution function can be used to represent the electron distribution in the Co nanoparticle. The model shown schematically in Fig. 6-3 (a) assumes that the magnetization vector of the nanoparticle is in a fixed orientation, whereas that of the right electrode is reversed by applying a magnetic field, leading to parallel (P) and anti-parallel (AP) alignments. The TMR is defined as TMR $\equiv 1 - R_P/R_{AP}$, where $R_P(AP)$ is the resistance of the whole system in the P (AP) alignment. The tunnel resistance and capacitance of each junction have been adjusted to reproduce the magnitude of the tunneling current and the period of the Coulomb staircase. The capacitances are taken to be $C_1 = 4.44$ aF and $C_2 = 3.00$ aF, where subscripts 1 and 2 correspond to the left and right junctions, respectively. The tunnel resistances for the parallel alignment were determined in the following way: first we decided that the tunnel resistance of the majority spin for parallel alignment at the left junction ($R^P_{1,\uparrow}$) was 25.0 GΩ, and the conductance bottleneck was placed at the left junction (PM / I / FM particle), assuming that $R^P_{1,\uparrow}$ was 10 times larger than $R^P_{2,\uparrow}$. The other resistances are given by

$$\begin{aligned} R^P_{1,\downarrow} = R^P_{1,\downarrow}(1+P_{Al})(1+P_{Partcle})/(1-P_{Al})(1-P_{Partcle}) &= 51.9G\Omega, \\ R^P_{2,\uparrow} = 0.1 \cdot R^P_{1,\uparrow} &= 250M\Omega, \\ R^P_{2,\downarrow} = 0.1 \cdot R^P_{1,\uparrow}(1+P_{Particle})(1+P_{Co})/(1-P_{Particle})(1-P_{Co}) &= 1.08G\Omega, \end{aligned} \tag{6.1}$$

where P_{Co}, $P_{Particle}$ and P_{Al} are the P_{tun} of the right electrode, the particle and the left electrode, and are assumed to be 0.35, 0.35 and 0, respectively. These considerably large resistances (GΩ) are reasonable for such a small tunnel junction consisting of nanoparticles. For the antiparallel alignment, tunnel resistances at the left junction were $R^{AP}_{1,\uparrow} = R^P_{1,\uparrow} = 25.0$ GΩ and $R^{AP}_{1,\downarrow} = R^P_{1,\downarrow} = 51.9$ GΩ. At the right junction, $D_{Particle,\downarrow} = D_{Particle,\uparrow}\,(1 - P_{Partcile})\,/\,(1 + P_{Particle})$, $D_{Co,\downarrow} = D_{Co,\uparrow}\,(1 - P_{Co})\,/\,(1 + P_{Co})$ and $R^P_{2,\uparrow} \propto (D_{Particle,\uparrow} D_{Co,\uparrow})^{-1}$produced

the following resistances:

$$R^{AP}_{2,\uparrow} = R^{P}_{2,\uparrow}(1+P_{Co})/(1-P_{Co}) \quad = \quad 519M\Omega,$$

$$R^{AP}_{2,\downarrow} = R^{P}_{2,\uparrow}(1+P_{Particle})/(1-P_{Particle}) \quad = \quad 519M\Omega. \tag{6.2}$$

When an external voltage is applied, electrons flow from the left to the right electrode. The current flowing in the junction is calculated using the master equation technique [21, 22]. By applying the charge conservation and Kirchhoff's law and by using the Fermi golden rule for the calculation of the tunneling Hamiltonian, we could write the tunneling rate for the i-th junction as follows:

$$\Gamma^{\pm}_{i,\sigma}(n) = \frac{1}{e^2 R_{i,\sigma}} \frac{E^{\pm}_i(n) + \Delta E^{\sigma}_F}{\exp\left(E^{\pm}_i(n) + \Delta E^{\sigma}_F/k_B T\right) - 1} \tag{6.3}$$

where i stands for the considered junction (i= 1, 2), σ stands for the direction of the spin, and the exponent $\pm$ indicates whether an electron is added or removed from the particle. Finally, the energy is written:

$$E^{\pm}_i(n) = (1+2n)\frac{e^2}{2C} \pm \frac{C_j}{C} eV (where j \neq i) \tag{6.4}$$

where $C = C_1 + C_2$, T is the temperature, and ΔE^{σ}_F the shift of the Fermi energy of the island due to spin accumulation for the σ-spin population. In the stationary regime, the transition rates for incoming and outgoing electrons cancel each other thes and the probability p(n) of finding n additional electrons in the central particle may then be calculated. Finally, the current is expressed as follows:

$$I = -e \sum_{\sigma} \sum_{n=-\infty}^{\infty} \left(\Gamma^{+}_{1,\sigma}(n) - \Gamma^{-}_{1,\sigma}(n)\right) \tag{6.5}$$

The spin accumulation in a Co nanoparticle is represented by the spin-dependent shift of the chemical potential for thegσgpin state ΔE^{σ}_F, which is determined by charge-neutrality and spin-conservation conditions. The former is given by $D_{\uparrow}\Delta E^{\uparrow}_F = -D_{\downarrow}\Delta E^{\downarrow}_F$,where D_{σ} is the density of states at the Fermi level for spin σ. The latter is expressed as follows:

$$\frac{(I_{1,\sigma} - I_{2,\sigma})}{e} = \frac{D_{\sigma}\Omega}{\tau_{SF}} \Delta E^{\sigma}_F \tag{6.6}$$

where $I_{i,\sigma}$ is the current at the i^{th} junction (i= 1, 2) for spin σ, Ω is the volume of the particle, τ_{SF} is the mean spin relaxation time in a nanoparticle defined as $\tau^{-1}_{SF} = (\tau^{-1}_{\uparrow} + \tau^{-1}_{\downarrow})/2$, and τ_{σ} is the spin relaxation time of electrons with spin σ. For a ferromagnet, $\tau_{\uparrow}$ and $\tau_{\downarrow}$ are not the same but satisfy the detailed balancing equation, $D_{\uparrow}/\tau_{\uparrow} = D_{\downarrow}/\tau_{\downarrow}$. The tunnel current is obtained by solving the master equation, charge-neutrality and spin-conservation conditions, self-consistently [14, 15, 27, 36].

We first show the results of numerical calculation assuming an infinite spin relaxation time in Fig. 6-3 (b), (c) and (d). The significant effect of the spin

accumulation is found in these results. Fig. 6-3 (b) shows the Vdependence of the chemical potential shifts ΔE_F^σ for the majority and minority spins in the P and AP alignment. It shows a sawlike oscillation with a period close to that of the Coulomb staircase shown in Fig. 6-3 (c). The important point is that the difference in the energy shift ΔE_F^σ for each alignment and spin leads to a splitting of the discrete charging levels $E_c^{\sigma,P(AP)}(n)$ for spin σ and P(AP) alignments, where $n$denotes the numbers of the charge in the particle. $E_c^{\sigma,P(AP)}(n)$ is expressed as

$$E_c^{\sigma,P(AP)}(n) = \frac{(n+1/2)e^2}{C_1} + \Delta E_F^{\sigma,P(AP)}(V). \tag{6.7}$$

The voltage corresponding to the step points of the Coulomb staircase is then accordingly split. In Fig. 6-3 (c), one can see that each $I-V$curve has a unique shape because ΔE_F^σ affects the tunnel conductance, and furthermore intersects around the step points of the staircase due to the split of $E_c^{\sigma,P(AP)}(n)$. This in turn leads to the periodical sign change of the Vdependence of TMR (TMR-Vcurve) with a period close to that of the Coulomb staircase as shown in Fig. 6-3 (d).

We also performed a calculation assuming an infinite spin relaxation time in the case of the converse arrangement of the conductance bottleneck; i.e., $R_{2,\uparrow}^P$ was fixed to be 25.0 GΩ and was assumed to be 10 times larger than $R_{1,\uparrow}^P$. The other resistances and capacitances are described in Fig. 6-4 (a). We show the results in Fig. 6-4 (b), (c) and (d). Though the V dependence of the chemical potential also appears as sawlike oscillations with a period of the Coulomb staircase, none of the $I-V$ curve intersect; thus no sign changes occur for TMR in the entire V range. These results indicate that the alternate sign change of TMR due to spin accumulation in the Co nanoparticle is reproduced when the conductance bottleneck is put at the junction of the PM / I / FM particle.

6.3 Evaluation of spin relaxation time

Fig. 6-5 shows the TMR-Vcurve for various values of the spin relaxation time τ_{SF}. Although the period of the oscillation does not depend on τ_{SF}, the shape of the TMR-Vcurve is quite different between the fast and slow spin relaxation regimes. The critical value of the spin relaxation time which divides the fast- and slow-spin relaxation regimes is about 100 ns, which corresponds to the interval between two successive tunneling events ($e/I \approx 100$ ns). In the fast-spin relaxation regime ($\tau_{SF} < 100$ ns), the TMR-Vcurve shows sharp positive peaks at the step points of the Coulomb staircase. On the contrary, in the slow spin relaxation regime ($\tau_{SF} > 100$ ns), sharp *negative* peaks appear at the same step points of the staircase, and broad positive bumps appear between two successive negative peaks. In Fig. 6-6 (a), (b), (c) and (d), we show cross-sections of Fig. 6-5 at $\tau_{SF} = 1$ ns, 10 ns, 150 ns and infinity, respectively. At $\tau_{SF} = 1$ ns, in the fast-spin relaxation regime, we have sharp positive peaks at V= 18,53,88, and 123 mV, where the tunneling current shows steps. The TMR-

Vcurve maintains the same shape as far as the spin relaxation time $\tau_{SF} < 1$ ns. However, at $\tau_{SF} = 10$ ns, one can see that dips which take negative TMR values appear at the step points of the Coulomb staircase. At $\tau_{SF} = 150$ ns, the TMR shows alternate sign changes with moderate amplitude reaching a maximum at infinite τ_{SF}. The negative peaks associated with the steps of the Coulomb staircase provide clear evidence of spin accumulation in Co nanoparticles [15, 27]. Finally as shown in Fig. 6-7, the experimentally observed TMR curve is well reproduced by choosing the spin relaxation time to be $\tau_{SF} = 150$ ns.

The present TMR experiments have shown that the tunnel current through nanoparticles is drastically affected by spin accumulation, and have revealed that the TMR exhibits a sign change at the step points of the Coulomb staircase. Although the spin relaxation mechanism of the magnetic nanoparticle is not well understood at present, there are some candidates for the cause of such a dramatic increase of the spin relaxation time. One is the quantization of energy levels, which is the most characteristic feature of nanoparticles with diameters of 1∼5nm [99-102]. The discrete energy level spacing in Co nanoparticles having a mean diameter of ∼2.5 nm is estimated to be about 2 meV, which is larger than the thermal fluctuation at 4.2 K (∼0.4 meV). The discreteness of the energy levels due to the zero dimensionality of nanoparticles leads to strong suppression of spin-flip scattering by the spin-orbit interaction in the nanoparticles [103, 104]. Mitrikas *et al.* have studied the spin-lattice relaxation of paramagnetic nanoparticles embedded in amorphous (SiO_2) and a crystalline (TiO_2) matrices [105]. They showed that the spin lattice relaxation (SLR) is blocked due to the amorphous phase of the matrix. Although their nanoparticle is not ferromagnetic, the blocking of the SLR is another candidate for the strong enhancement of the spin relaxation time in our sample because the insulating Al-O matrix is in an amorphous phase. Furthermore, the spin-flip mechanisms due to the interaction with magnons in a nanoparticle are also suppressed because of the size quantization of magnon excitations [106].

Recently, further experimental studies on spin accumulation in paramagnetic Au nanoparticles have been performed [68, 72]. Observation of non-zero TMR is attributed to the spin accumulation in Au nanoparticles in an FM / I / Au particles / I / FM structure, which should not show TMR in the framework of Julliére model. Although these studies did not mention the spin relaxation time in Au nanoparticles, the nano-ampere order of the observed current suggested a nano-second order for the spin relaxation time (e/I). It is suggested to be enhanced even in the Au nanoparticles. All of these particular features of nanoparticles can lead to an extremely long spin relaxation time and a striking spin accumulation effect on TMR. To determine the dominant mechanism of spin relaxation in nanoparticles, further studies investigating the dependence of spin relaxation time on variables such as the temperature, the material of the insulating matrix and particle size are needed. We note that the results shown here are promising for the potential application of nanoparticles as basic elements of spin-electronic devices.

7. Summary

We have reviewed studies on spin-dependent transport in systems containing ferromagnetic nanoparticles. In a tunnel junction with a ferromagnetic nano-island and electrode, spin-dependent single-electron tunneling (SD-SET) gives rise to remarkable tunnel magnetoresistance (TMR) phenomena. We studied magnetotransport properties in both sequential tunneling and cotunneling regimes of SET and found the enhancement and oscillation of TMR.

The self-assembled ferromagnetic nanoparticles we used in this study consisted of a Co-Al-O granular film, with cobalt nanoparticles embedded in the Al-O insulating matrix. In Ch. 3 we showed the preparation methods, and basic transport and magnetic properties of the films. A $Co_{36}Al_{22}O_{42}$ film prepared by the reactive sputtering method produced a TMR ratio reaching 10 % and superparamagnetic behavior at room temperature. The fitting of the magnetization curve to that of the calculation from the Langevin function revealed the distribution of particle sizes ranging from 2 nm to 5 nm. The TMR ratio exhibited an anomalous increase at low temperatures but no significant indication of change with bias voltage. In Ch. 4, we showed that the anomalous increase of the MR indicated evidence for higher-order tunneling (cotunneling) between large granules through intervening small granules. We emphasize that the existence of higher-order tunneling is a natural consequence of the granular structure, since broad distribution of granule sizes is an intrinsic property of granular systems.

In Ch. 5, we concentrated on SD-SET properties in a sequential tunneling regime. In order to study it, the tunnel paths between electrodes had to be restricted because the film contains a large number of particles of different sizes. We fabricated two types of device structures with Co-Al-O film using focused ion-beam milling or electron-beam lithography techniques. One is a granular nanobridge structure: point-shaped electrodes separated by a very narrow lateral gap filled with Co-Al-O granular film. The other is a current-perpendicular-to-plane (CPP) geometry structure: a thin Co-Al-O granular film sandwiched by ferromagnetic electrodes with the current flowing in the direction perpendicular to the film plane through a few Co particles. We measured the current-bias voltage curves in these samples, and found the enhancement and oscillation of TMR due to spin-dependent SET in a sequential tunneling regime. We made a theoretical calculation employing the orthodox theory of SET and explained the enhanced TMR just above the Coulomb threshold voltage. In Ch. 6, we reported experimental evidence of the spin accumulation effect in Co nanoparticles leading to the oscillation of TMR with alternate sign changes. Furthermore, the spin relaxation time in Co nanoparticles was also evaluated by comparing the experimental results to numerical simulations. We discovered that the spin relaxation time in the nanoparticles is unprecedentedly enhanced up to more than the order of hundreds of nanoseconds, compared to that evaluated from the spin diffusion length of ferromagnetic layers in previous CPP-GMR studies, *i.e.*,the order of tens of picoseconds.

Although the spin relaxation mechanism of the magnetic nanoparticle is

not well understood at present, there are some candidates for cause of such a dramatic increase of the spin relaxation time: suppression of spin-flip scattering by spin-orbit interaction due to the discrete energy level spacing in the Co nanoparticle and/or blockade of spin-lattice relaxation due to the amorphous Al-O matrix. Further studies such as measuring the temperature dependence of spin relaxation time will clarify the mechanism of spin relaxation in nanoparticles.

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Figure captions

Fig. 2-1 Schematic diagram of a circuit including a single-electron tunneling (SET) double junction.

Fig. 2-2 Current (I) - bias voltage (V) characteristics of a SET junction (a) with no asymmetry [of tunnel] resistances, and (b) with strong asymmetry of tunnel resistances.

Fig. 2-3 Schematic diagram of a double tunnel junction to explain chemical potential shift due to spin accumulation in the ferromagnetic nanoparticle.

Fig. 3-1 Schematic illustration of a sputtering method for preparing insulating granular films: (a) reactive sputtering, (b) sputtering with a composition target and (c) tandem deposition with plural targets.

Fig. 3-2 (a) Plan view and (b) cross-sectional view of transmission electron microscopy (TEM) micrographs for a $Co_{46}Al_{19}O_{35}$ film.

Fig. 3-3 High-resolution electron microscopy (HREM) micrograph for $Co_{36}Al_{22}O_{42}$ granular film.

Fig. 3-4 Temperature (T) dependence of electrical resistivity (ρ) for Co-Al-O films of different compositions: $Co_{54}Al_{21}O_{25}$, $Co_{52}Al_{20}O_{28}$, $Co_{46}Al_{19}O_{35}$, and $Co_{36}Al_{22}O_{42}$.

Fig. 3-5 (a) Magnetic-field dependence of magnetization ($M-H$) and (b) temperature dependence of magnetization ($M-T$) for the $Co_{36}Al_{22}O_{42}$ film. In (b), $M-T$ curve of field cool (FC) was measured at $H = 20$ Oe.

Fig. 3-6 Magnetic-field dependence of electrical resistivity (MR curve) measured at (a) room temperature and (b) 4.2 K. Magnetoresistance (MR) ratio shown in the left axis was estimated from the definition: MR $= \Delta\rho$vρ_{max}.

Fig. 3-7 The result of particle size distribution of a $Co_{46}Al_{19}O_{35}$ film estimated from superparamagnetic behavior. (a) Result of fitting calculated magnetization curves to experimental results at $T = 200$ and 293 K. (b) The size distribution which gives the best fit in (a).

Fig. 4-1 Temperature (T) dependence of the tunnel magnetoresistance (TMR) ratio for Co-Al-O films of various compositions: $Co_{54}Al_{21}O_{25}$, $Co_{52}Al_{20}O_{28}$, $Co_{46}Al_{19}O_{35}$, and $Co_{36}Al_{22}O_{42}$. Solid curves (a, b, c, and d) represent the theoretical magnetoresistance ratio given by Eq. (4.2) with spin polarization P; a: $P = 0.306$; b: $P = 0.290$; c: $P = 0.275$; d: $P = 0.250$.

Fig. 4-2 Schematic illustrations of current-perpendicular-to-plane (CPP) geometry sample where a 1 μm thick $Co_{36}Al_{22}O_{42}$ granular film was sandwiched between upper and lower Au-Cr electrodes.

Fig. 4-3 Bias voltage (V_b) dependence of ρ at H = 0 (a) and V_b dependence of TMR (b) for a CPP geometry sample with $Co_{36}Al_{22}O_{42}$ measured at 4.2 K. Closed circles represent the experimental results and solid curves represent the theoretical ones using Eq. (4.6) with$T$ = 4.2 K and N_g = 140.

Fig. 4-4 (a) Schematic illustration of granular structure and a higher-order tunneling process where a charge carrier is transferred from the charged large granule (left), via the two small ones, to the neutral large one (right). (b) Model structure used for the calculation of conductivity.

Fig. 4-5 Temperature (T) dependence of electrical resistivity (ρ) for Co-Al-O films of different compositions: $Co_{54}Al_{21}O_{25}$, $Co_{52}Al_{20}O_{28}$, $Co_{46}Al_{19}O_{35}$, and $Co_{36}Al_{22}O_{42}$. Solid lines represent the theoretical results given by Eq. (4.2) with charging energy E_c; $Co_{36}Al_{22}O_{42}$: E_c / k_B = 110 K; $Co_{46}Al_{19}O_{35}$:E_c / k_B = 25 K; $Co_{52}Al_{20}O_{28}$: E_c / k_B = 18 K; $Co_{54}Al_{21}O_{25}$: E_c / k_B = 9 K.

Fig. 5-1 (a) Scanning tunneling microscopy (STM) topographic image and (b) current – bias voltage characteristics based on scanning tunneling spectroscopy (STS) measurements at room temperature for a $Co_{36}Al_{22}O_{42}$ film.

Fig. 5-2 (a) Schematic view of an insulating granular nanobridge. (b) Scanning ion microscopy image of the NbZrSi electrodes separated by a nanometer-sized lateral gap. The length (l) is 30 nm and the width (w) is 60 nm.

Fig. 5-3 (a) Current – bias voltage ($I - V_b$) characteristics and (b) V_b dependence of TMR measured at 4.2 K for a sample of w = 60 nm, l = 30 nm and t = 7.5 nm. In (a), the solid and dashed curves represent $I - V_b$ curves in a magnified current range at H = 0 and 10 kOe, respectively. $I - V_b$ curves throughout the measured current range are shown in the inset.

Fig. 5-4 (a) Current – bias voltage ($I - V_b$) characteristics and (b) V_b dependence of TMR measured at 4.2 K for a sample of w = 700 nm, l = 40 nm and t = 15 nm. Viewgraphs are shown in the same form as in Fig. 5-3.

Fig. 5-5 V_p vs. V_{th} for the various samples. V_p is the voltage where the TMR shows the maximum.

Fig. 5-6 (a) Schematic illustration and equivalent circuit of the calculation model. The conducting path in the contact is modeled by a parallel circuit of 20 triple-tunnel-junctions, assuming the tunnel resistance between an electrode and a particle (R_{ep}), tunnel resistances between particles (R_{pp}) and junction capacitances (C_{ep} and C_{pp}). These parameters are assumed to be distributed around

the mean values, *i.e.*, $R_{ep} = (1 \pm \delta)\overline{R}_{ep}$, $R_{pp} = (1 \pm \delta)\overline{R}_{pp}$, $C_{ep} = (1 \pm \delta)\overline{C}_{ep}$, and $C_{pp} = (1 \pm \delta)\overline{C}_{pp}$, where δ is the deviation from the typical value. (b) The numerical calculation results (solid curve) and experimental results (dashed curve).

Fig. 5-7 Schematic illustrations of (a) the CPP geometry sample, and (b) the process of making a contact area by FIB etching.

Fig. 5-8 (a) Current – bias voltage ($I - V_b$) curves and (b) bias-voltage dependence of TMR measured at 4.2 K for a CPP geometry sample with a 0.5 x 0.5 μm^2 contact area. In (a), the solid and dashed curves represent $I - V_b$ curves at $H = 0$ and 10 kOe, respectively.

Fig. 6-1 Schematic illustration of a sample with pillar structure, prepared for the current-perpendicular-to-plane (CPP) measurement. It consists of Al bottom electrode / Al-O / Co-Al-O granular film / Co top electrode / Pt microfabricated by electron-beam lithography and Ar ion milling process to reduce the contact area down to 0.4 x 0.4 μm.

Fig. 6-2 Magnetotransport properties measured at 4.2 K in an Al / Al-O / Co-Al-O / Co sample of sub-micron sized area. (a) Current (I) - bias voltage (V) curves and (b) V dependence of the tunnel magnetoresistance (TMR). In (a), the gray and black solid curves represent a clear Coulomb staircase at zero magnetic field ($H = 0$) and applied field ($H = 10$ kOe), respectively. (c) The magnetic field dependence of electrical resistance (MR curves) at $V = 0.05$ V and 0.12 V at which TMR shows negative and positive values, respectively.

Fig. 6-3 Numerical calculation results considering the spin accumulation effect on TMR. The model assumes that a spin relaxation time in the ferromagnetic island is infinite and that a conductance bottleneck exists at the junction between the ferromagnetic island and the paramagnet electrode. (a) Schematic illustration of the model: paramagnet / ferromagnet / ferromagnet double tunnel junction. (b) V dependence of the chemical potential splitting ΔE_F^σ, which is caused by the spin accumulation. (c) Current (I) - bias voltage (V) curves in the anti-parallel (AP, dashed line) and parallel (P, solid line) alignments. (d) V dependence of the tunnel magnetoresistance (TMR).

Fig. 6-4 Numerical calculation results in the case of converse arrangement of the conductance bottleneck, i.e., $R_{2,\uparrow}^P P$ is fixed to be 25.0 GΩ and to be 10 times larger than $R_{1,\uparrow}^P$. (a) Schematic illustration of the model: paramagnet / ferromagnet / ferromagnet double tunnel junction. (b) V dependence of the chemical potential spliting ΔE_F^σ. (c) Current (I) - bias voltage (V) curves in the anti-parallel (AP, dashed line) and parallel (P, solid line) alignments. (d) V dependence of TMR.

Fig. 6-5 Surface plot of the TMR, which is calculated by the orthodox the-

ory, as a function of V and τ_{SF}.

Fig. 6-6 V dependence of TMR for various values of the spin relaxation time τ_{SF}: (a) 1 ns, (b) 10 ns, (c) 150 ns and (d) infinity.

Fig. 6-7 V dependence of TMR of [the] calculation result ($\tau_{SF} = 150$ ns) and experimental TMR. The TMR curve is well reproduced by choosing the spin relaxation time to be $\tau_{SF} = 150$ ns.


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